⑲日本国特許庁

公開特許公報

⑪特許出願公開

昭52—151362

⑤1Int. Cl².	識別記号	⑤2日本分類	庁内整理番号	⑬公開 昭和52年(1977)12月15日
B 29 D 3/02		25(5) J 12	7139—37	

発明の数 3
審査請求 有

(全 6 頁)

⑤4引揃えプリプレグ及びその製造法

⑳特願 昭51—68373
㉒出願 昭51(1976)6月11日
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明細書

1. 発明の名称

引揃えプリプレグ及びその製造法

2. 特許請求の範囲

(1) 一方向に並行するマルチフイラメントの繊維の束の複数個を互いに隣接し、かつその繊維長方向にこれら束間及び束内でフイラメントの一部又は大部が他のフイラメントと絡らみ、かつ繊維が樹脂で含浸してなる引揃えプリプレグ。

(2) マルチフイラメントの繊維の束の複数個を一方向に並行して互いに隣接させ、得られる繊維の束の集合体に高圧流体を吹き付け、吹き付け時又は吹き付け後にその繊維の束の集合体に樹脂を含浸させることを特徴とする引揃えプリプレグの製造法。

(3) 流体が水、水と空気との混合物、有機溶媒及び合成樹脂のいずれかである特許請求の範囲第2項の引揃えプリプレグの製造法。

(4) 流体の圧力が50～500 kg/cm²である特許請求の範囲第2項又は第3項記載の引揃えプリプレグの製造法。

(5) マルチフイラメントの繊維の束の複数個を一方向に並列して互いに隣接させ、得られる繊維の束の集合体を連続的に巻取りたがら、この繊維の束の移行する方向に対して直角の方向に往復運動をする高圧流体を噴出するノズルから高圧流体を前記繊維の束の集合体に吹きつけ、この繊維の束と束との間及び束内でフイラメントの一部又は大部を他のフイラメントと絡らませ、その繊維の束の集合体を前記高圧流体の吹き付け中又は吹き付け後に樹脂を含浸させることを特徴とする引揃えプリプレグの製造法。

(6) 流体が水、水と空気との混合物、有機溶媒及び合成樹脂のいずれかである特許請求の範囲第5項記載の引揃えプリプレグの製造法。

(7) 流体の圧力が50～500 kg/cm²である特許請求の範囲第5項又は第6項記載の引揃えプリプレグの製造法。

8. 発明の詳細な説明

本発明は繊維強化プラスチックの成形材料として用いられる引揃えプリプレグに関するものである。

繊維強化プラスチック用のプリプレグは不織布状、ヤーン状、クロス状又はチョップストランド状の繊維、或は一方向に引揃えた繊維、又はこれらを組み合わせたものに熱硬化性樹脂を含浸したもので、得られたプリプレグはこの製造に用いられた繊維によつてそれぞれの特徴が生じ、その特徴に応じて各種の用途に向けられている。

これらのプリプレグのうち、一方向に引揃えた繊維を用いて得たプリプレグは容易に薄いシート状、テープ状のものが得られるため長尺の板状体、積層板等の成形材料として好適で、例えばゴルフのクラブシャフト、スキーのボディ等のレジャースポーツ用品や自動車、航空機材などの高強度複合材料に用いられている。

従来、この種のプリプレグは一方向に引揃えた

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成形品としての品質が低下する欠点を有している。

さらに一方向引揃えプリプレグを成形し、かつその成形品の樹脂を硬化させて得られる繊維強化プラスチック製品の引揃え方向とその直角方向の強度は硬化樹脂自体の強度及び硬化樹脂と繊維との接着力によつて決定されるが、従来法による一方向引揃えプリプレグは前述したように硬化樹脂と繊維との接着力のみによつて決まり比較的弱いので、このプリプレグを用いた繊維強化プラスチック製品の引揃え方向とその直角方向の強度は高い値を取ることが困難である。とくに上記のように繊維の束と束との間に隙間が生じたプリプレグを用いて得た製品の強度が低下し、かつ仕上り（外観的）にも劣り、さらに製品の特性に大きなバラツキが生ずるなどの問題点があつた。

本発明の目的は機械的ストレス及び又は熱変化によつて繊維と樹脂との結合力が低下せず、マルチフイラメントの繊維の束と束との間に隙間

(5)

たマルチフイラメントの繊維の束に樹脂を含浸し、その繊維の束の複数個を同方向にそれぞれの束が互いに隣接するように並べてこれら繊維の束と束とをこれら束に含浸させた樹脂によつて接合してシート状又はテープ状の形状に成形することにより得られている。

この従来方法により得られる一方向引揃えプリプレグは未硬化の樹脂の結合力だけで一方向に並行するマルチフイラメントの繊維の束と束とが接合されているので、このプリプレグは機械的ストレス、熱変化に対する抵抗力が小さく、これら条件が加わることによつて繊維の束と束との結合力が弱まる。その結果従来のプリプレグは長期間の保存、使用のさいの温度変化によつてプリプレグの繊維の束と束との間に隙間を生じ、ときには層状的に離間するにいたり、また通過したり、このプリプレグを用いて成形品を製作するさいにも機械的ストレス，熱変化によつて繊維の束と束との結合力が弱まり隙間や離間が生じ易くプリプレグとして品質、又は

(4)

強度が生じにくい引揃えプリプレグ及びその製造法を提供するにある。

本発明の他の目的は取扱い、通過、成形加工又は保管によつて品質低下しない引揃えプリプレグ及びその製造法を提供するにある。

本発明のさらに他の目的は繊維強化プラスチック製品に用いた場合、その製品の繊維引揃え方向とその直角方向の強度を増大し得、かつその他の諸特性をバラつかせない引揃えプリプレグ及びその製造法を提供するにある。

本発明者は前記目的を達成するため種々研究した結果完成したもので、その引揃えプリプレグの特徴は一方向に並行するマルチフイラメントの繊維の束の複数個を互いに隣接し、かつその繊維の束内及び束間でフイラメントが他のフイラメントと交絡し、樹脂で含浸されてなるものである。

本発明に用いられるマルチフイラメントの束はフイラメントが多数本集合してなる繊維の束であつて、連続した長繊維の束からなるヤーン

(6)

又はトウ等が好ましい。

この繊維には従来の引揃えプリプレグに用いられる繊維が用いられ、これを示せば下記の通りである。

(1) 有機繊維：ナイロン（ポリアミド系）、レーヨン（セルロース系）、ビニロン（ポリビニルアルコール系）等

(2) 有機耐熱繊維：芳香族ポリマー、ポリベンズイミダゾール、ポリフルオロカーボン、ポリアミド、フェノール、ポリフェニレオキソジアゾール、ビスベンズイミダゾベンゾフェナンスロライン、ポリチアジアゾール、ポリフェニレントリアゾール、ポリピチアゾール、ポリイミド等の樹脂繊維

(3) 無機繊維：ガラス、窒化ホウ素、アルミナ、窒化ケイ素、アスベスト、ジルコニア、シリコンカーバイド、炭素（炭素質、黒鉛質、耐炎質を含む）等の繊維、

(4) 金属繊維：タングステン合金、ベリウム、銅合金、鉄、アルミニウム等の繊維、

ール、エチルアルコール、アセトン、トルエン、メチルエチルケトン等）及び合成樹脂等が用いられる。合成樹脂を用いる場合には繊維に含浸させる合成樹脂と同一であることが好ましく、また吹きつけるさい加温して粘度を下げたり、又は使用する合成樹脂にこれと相溶性の有機溶媒を添加したり、さらにまた有機溶媒以外の希釈剤（例えば塩化ビニル樹脂用可塑剤、高沸点溶剤、ポリプロピレングリコール、スチレンモノマー、ポリエチレン）を用いて流体の粘度を下げて吹きつけることが好ましい。

流体に水、又は水と空気との混合物を用いる場合には流体のコストが安く、流体の回収が全く必要とせず、また作業環境がよく環境汚染することがなく、操作や設備が簡単であるが一方有機溶媒や合成樹脂を用いた場合には流体を吹きつけ後の乾燥工程が簡単であるか又はこれを全く必要とせず、吹き付け工程に続いて連続してマトリックス用としての樹脂を含浸させることができる。特に合成樹脂を十分に吹き付けし

(5) 混合繊維：ホウ素（芯線ータングステン）、炭化ホウ素（芯線ータングステン）、シリコンカーバイド（芯線ータングステン、ホウ素）等の繊維

(6) (1)～(5)で示した繊維のうち二種以上組み合わせたもので、特に可撓性、強靭性に富むものが好ましい。

マルチフィラメントの繊維の束内及びその束とその束に近接する束との間でフィラメントを他のフィラメントと交錯させるには複数個の繊維の束を互いに隣接する束が交り合つて厚みが不均一にならないように密着させて一定巾のシート又はテープ状とし、かつそれぞれの束が処理中に乱んで配列が乱れないよう適度に張りながら（例えば0.02～0.65 g/d の張力を繊維長方向にかける。）、これら配列した繊維の表面に高圧の流体を吹きつける機械的な衝撃を与えることにより得られる。

このさいに用いる高圧流体には、水、水と空気との混合物、有機溶媒（例えばメチルアルコ

た場合には、繊維を改めて樹脂に浸漬することなく、吹き付けて得られたものを単にローラー掛けを行う程度で繊維の束の内部に樹脂を含浸させることができる。

繊維束面に高圧流体を吹きつけるには繊維引揃え方向に対して直角に繊維束面上適当な間隔に設けたノズル孔から噴射する方法が採られる。

ノズル孔径の太さ及びその繊維までの間隔及びノズル数はフィラメントの太さ及び繊維層の厚みなどによつて異なるが、ノズル孔径は1㎜以下、特に0.5～0.05㎜が好ましいが、これが余り太くなると多数のフィラメントが同時に変位して結びため、繊維の束が乱れ易く、厚さも不均一となり引揃えの効果が失なわれる。

ノズル孔と繊維束面との距離は高圧流体の圧力、繊維のノズル孔に対する相対移動速度、繊維フィラメントの太さ及び束の厚さ等によつて定められるが1～15㎜程度が目安となる。

高圧流体の圧力もまたノズル孔の太さ、ノズル孔と繊維束面との距離、繊維のノズル孔に対

する相対移動速度フイラメントの太さ及び繊維の束の厚みなどによつて限定されるが5.0～400kg/cm²であることが好ましい。圧力が50kg/cm²未満であるとフイラメントの転位が少なくて繊維の束と束との係合が不十分であり、また400kg/cm²を超えるとフイラメントの破断が多くケバ立ちが激しくなる。

高圧流体を繊維束面に吹きつけるさい、ノズルを固定して繊維の束を引揃え方向に移動させるとともに、その直角方向にも移動させてもよく、またこの逆にノズルを移動させて繊維束を固定してもよい。ノズル又は繊維束の移動速度は1～10m/min程度が適切である。繊維束を連続的に処理する場合、第2図に示すように繊維束をエンドレスに張架させながら巻取り、そのさいに巻取り方向に対して直角の方向に往復運動をさせながら繊維束面に圧力流体を噴射させることにより行なわれる。

含浸に用いられる樹脂にはフエノール樹脂、不飽和ポリエステル樹脂、エポキシ樹脂等の熱

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具の取り付けも簡単で繊維に対して張力を掛け易いのでフイラメントの絡み度合を自由に調整することができる。

つぎに本発明の引揃えプリプレグの製造法の一実施態様を図について説明する。

第1～第2図においてクリール7より引揃えたマルチフイラメント束1を巻取りドラム14に巻取り、このマルチフイラメント束群1を押えローラ11、12、13によつて受け皿9の中を通過させ、その通過のさいマルチフイラメント束の移行する方向に対して直角に、かつそのマルチフイラメント束面から適当な距離を保つて設けられたノズル孔8よりポンプ8によつて高圧流体をフイラメントの束面に吹きつける。受け皿9は押えローラ12、13間で繊維の束に吹きつけられた流体を収容する容器で図には示さなかつたがこの受け皿9には流体の排出口が設けられ、必要に応じて流体を高圧ポンプ8に戻して再び使用する。またこの受け皿9には繊維束の移行面に並行して当て板3を設け一度

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硬化性樹脂、ポリイミド樹脂、ポリベンズイミダゾール樹脂、ポリフエニレン樹脂、フリーデルクラフト樹脂等の耐熱性樹脂が用いられ、使用するに当つて粘度を低下させるため加温したり、またこれに有機溶媒及び又は希釈剤を添加して用いられる。

さらに繊維の束面に高圧流体を吹きつけるさい、その高圧流体が吹きつける繊維の束面の裏面に近接して、かつこの繊維の束面と平行に当て板を設け、この当て板によつてさらに一度高圧流体をはね返して再び繊維の束に衝突させるとフイラメントの転移が能率よく行なわれる。

この当て板には表面がほぼ平滑で流体を反射し得るようにされ、金属、プラスチック、ガラス、木、硬質ゴム等で製作される。構造は全く穴部を有しない平板又は円筒、又は第3～第6図に示すように網目、格子状もしくは短冊状の穴部を有するものが用いられる。

当て板を用いると繊維の束をこの上に配列して、この当て板を利用するので繊維の束の押え

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繊維の束に吹きつけた高圧流体をこれに当ててはね返し再び繊維のフイラメントに当ててそれを配位させ、高圧流体を効率よく使用する。

当て板は高圧流体を反射し、かつこれを反射し得る強度を有するもので、この実施態様には第3図～第6図に示すように平板、円筒状を含めて、平板に多数の穴を設けて高圧流体が繊維の束内を通過し易くし、繊維のフイラメントを横方向だけでなく、繊維の束の厚み方向にも繊維のフイラメントを配位させこれらを絡み合わせることができる。

すなわち、第3図は平板状の当て板3aを示し、第4図は平板状の当て板3bに短冊状の穴部5bを設けたもの、第5図は平板状の当て板3cに網目状の穴部5cを設けた当て板の平面図を示し、第6図は円筒状の当て板3dを用いて繊維束14にノズル6dから高圧流体を吹きつけている装置の正面図を示す。この穴を設けた当て板は厚みが大きいプリプレグの製造に適している。

また、第1〜第2図において6はノズルで繊維束の移行する方向に対して直角に往復運動させる。

高圧流体によつてフィラメントが繊維軸と直角な方向に転位して絡んでシート状となつた繊維の束を必要に応じて乾燥炉10に移行し、ここで乾燥させたのち、その繊維の束を樹脂含浸槽11に入れその中の樹脂浴に浸漬させる。ついでローラ12によつて樹脂の含浸を十分に行なうとともにその樹脂の含浸量を調整する。さらに必要に応じて加熱炉13に入れ、樹脂含浸繊維に含まれる有機溶媒成分を揮発させ、かつ樹脂の重縮合度を高め最後に巻取り機14により引揃えプリプレグが得られる。加熱炉13の中で加熱した成形体は離型紙を挟めることが好ましい。

本発明の引揃えプリプレグは第7図に示すようにこれが構成されている繊維の束1aと束1aとの間、及びその束内でフィラメント2aの一部又は大部が転位して絡み合つているので、第8図に示す従来品とは異なり機械的ストレス及

(9)

び熱ストレスによつて繊維と樹脂との結合力が低下せず、これにともない繊維の束と束との間に間隙が生じないので、取扱い、運搬加工、又は保管によつて品質が低下しない。またこれを用いて繊維強化プラスチック製品とした場合、繊維長方向の強度低下がほとんどなく、従来法に得られた製品に比して繊維の引揃え方向及びその直角方向の強度が1.5〜4倍も増大させることができる。

つぎに本発明の実施態様を実施例で説明するが本発明はこれらによつて限定されるものではない。

実施例1

12000フィラメント、4800デニールの炭素繊維(引張強度340kg/mm²、引張弾性率20t/mm²)のフィラメントヤーンを100本を木製の平板の上に0.10g/dの張力を掛けて引揃えて並べた、この引揃えたヤーンの上を次の条件で水のジェット流を吹き付けた。

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水のジェット流の条件

ノズル直径　0.2mmφ

圧　　力　max 200kg/cm²(40回/分の脈流)

ノズルの先端とヤーンとの距離　8m/m

ノズルの個数　1ケ

ノズル移動速度　4.5m/min(引揃え方向と直角の方向へ移動し、5m/mの巾で全面に吹き付けた)

水のジェット流の吹き付け工程後、処理した炭素繊維の一部を採り、その特性を測定したが吹き付け工程前と比較して引張強度、引張弾性率には全く低下は見られなかつた。

繊維の長さ方向に対して直角方向の束間破断強度は吹き付け工程前では0であつたが吹き付け工程後では200g/1cm巾となつた。

このようにして得られたシートを100℃、2時間乾燥後メチルエチルケトンを溶剤としたエポキシ樹脂(エピコート#828,100

(11)

部 BF_3 MEA 3 PHR、MEK 150PHR)に含浸し、ついで120℃で15分間乾燥した。この0.1mm厚の引揃えプリプレグシートを1方向で積層し150×80×3mmの寸法で成形した。この時の強度は繊維方向引張強度(σy)は193kg/mm²、繊維と直角方向引張強度(σx)は8.4kg/mm²であつた。この時の繊維体積含有率は61%であつた。

実施例2

水のジェット流の圧力を400kg/cm²とした以外は実施例1と同じ条件で、炭素繊維を処理して引揃えプリプレグシートを得た。これを実施例1に準じて積層し実施例1の場合と同じサイズで成形した。

このもののσyは169kg/mm²、σxは14.1kg/mm²であつた。

実施例3

水のかわりにメチルエチルケトンに35%のエポキシ樹脂を含む溶液(硬化剤も含む、粘度20℃で25cp)を用いてジェット流を

(12)

吹き付けた他は実施例1と同様の条件で炭素繊維を処理して引揃えプリプレグシートを得た。これを実施例1に準じて積層し、実施例1の成形品と同じ寸法に成形した。このもののσyは1.9 kg/mm²、σxは7.6 kg/mm²であつた。

比較例1

実施例1に用いた炭素繊維を、水のジェット流を用いない以外は実施例1と同じ条件で処理し、得られた引揃えプリプレグシートを、さらに実施例1に準じて積層し実施例1の成形品と同じ寸法に成形した。このもののσyは1.5 kg/mm²、σxは3.8 kg/mm²であつた。

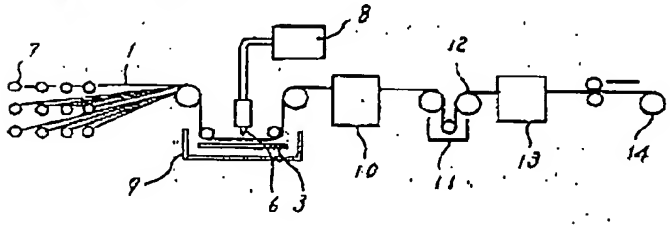
4. 図面の簡単な説明

第1図は本発明の引揃えプリプレグの製造法の一実施態様の工程説明図、第2図は高圧流体を繊維束に吹きつけるさいの装置の斜視図、第3図～第5図は各種当て板の平面図、第6図は円筒状の当て板を用いて繊維束にノズルから高圧流体を吹きつけている装置の正面図、第7図は本発明の引揃えプリプレグの縦断面図及び第8図は従来品の引揃えプリプレグの縦断面図を示す。

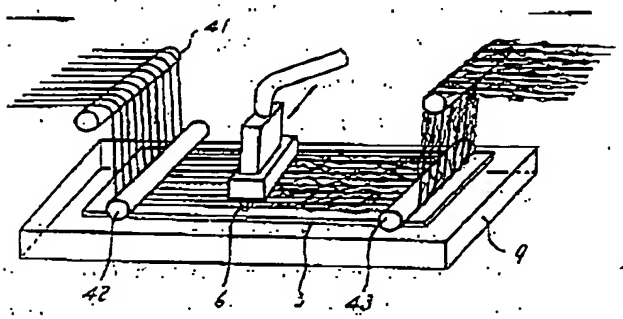
1、1e、1f：束
2e、2f：フィラメント
3、3a、3b、3c、3d：当て板
41、42、43：抑えローラー
5b、5c：穴
6、6d：ノズル
7：クリール
8：高圧ポンプ
9：受け皿
10：乾燥炉
11：含浸槽
12：ローラー
13：加熱炉
14：巻取り器

特許出願人　工業技術院長松本敏信
日本カーボン株式会社

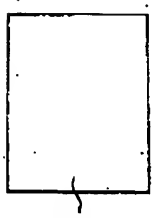
第1図



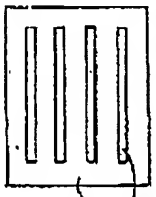
第2図



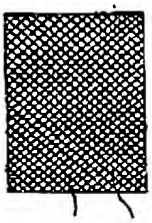
第3図



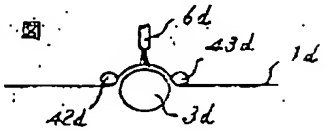
第4図



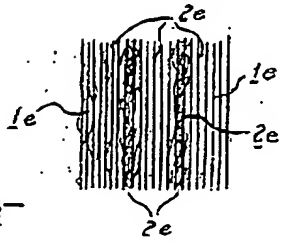
第5図



第6図



第7図



第8図

Mr. Snider:
The data below belongs to the Fax sent on December 7, 2005. TOGAWA & CO.

(English Translation of Japanese Patent Application Laid-open No.52-151362)

A PRE-IMPREGNATION SHEET COMPRISING A PLURALITY OF MULTI-FILAMENT BUNDLES ALIGNED WITH EACH OTHER AND A METHOD OF PRODUCING THE SAME

WHAT IS CLAIMED IS:

1. A pre-impregnation sheet comprising a plurality of multi-filament bundles aligned with each other wherein said bundles are uni-directionally disposed in parallel and one of some and most of monofilaments of said bundles respectively are intermingled with each other longitudinally along a moving course of said bundles and latitudinally with regard to said course and said monofilaments are impregnated with a resin.

2. A method of producing a pre-impregnation sheet comprising a plurality of multifilament bundles aligned with each other comprising the steps of uni-directionally disposing said plurality of multifilament bundles in parallel and blowing a high-pressurized fluid to a collection of said bundles in alignment and impregnating said collection with a resin one of when and after said fluid is blown over thereto.

3. A method of producing a pre-impregnation sheet comprising a plurality of multifilament bundles aligned with each other according to claim 2 wherein said fluid is one selected from water, mixture of water and air, an organic solvent and a synthetic resin.

4. A method of producing a pre-impregnation sheet comprising a plurality of multifilament bundles aligned with each other according to claim 2 or 3 wherein a pressure applied to said collection by said fluid ranges from 50 to 500 Kg/cm^2.

5. A method of producing a pre-impregnation sheet comprising a plurality of multifilament bundles aligned with each other comprising the steps of uni-directionally disposing said bundles in parallel and blowing a high-pressurized fluid to a collection of said bundles from a nozzle reciprocally moving crosswise with regard to a moving course of said collection while continuously winding up said collection in alignment so

as to intermingle one of some and most of monofilaments of said bundles respectively with each other longitudinally along a moving course of said bundles and latitudinally with regard to said course and impregnating said collection with resin one of when and after said fluid is blown over thereto.

6. A method of producing a pre-impregnation sheet comprising a plurality of multifilament bundles aligned with each other according to claim 5 wherein said fluid is one selected from water, mixture of water and air, an organic solvent and a synthetic resin.

7. A method of producing a pre-impregnation sheet comprising a plurality of multifilament bundles aligned with each other according to claim 5 or 6 wherein a pressure applied to said collection by said fluid ranges from 50 to 500 Kg/ cm^2.

(DETAILED DESCRIPTION OF THE INVENTION)

The invention relates to a pre-impregnation sheet comprising a plurality of multifilament bundles aligned with each other that is adopted for a forming material of a fibers reinforced plastic product.

The pre-impregnation sheet used for producing such plastic product is arranged such that non-woven fibers, yarn fibers, cloth fibers and chopped strand fibers, uni-directionally aligned fibers or such fibers as combining some of those fibers are impregnated with a thermoset resin, which pre-impregnation sheet as obtained has characteristics varied according to the type of fibers in use and is used in various fields according to such characteristics in need.

Among such sheets as mentioned above, that obtained by use of uni-directionally aligned fibers is easier to be formed into a thin sheet or tape shape so as to be optimum for the material for a tube-like body or a laminate plate and so forth so that it is adopted for such complex material of high strength as used for producing such sports or leisure goods as a golf shaft, a ski board and the assembly parts of automobiles and airplanes and the like.

Conventionally, such pre-impregnation sheet as mentioned

above is produced by impregnating uni-directionally aligned multifilament bundles with a resin and disposing in parallel a plurality of those bundles side by side so as to join the adjacent bundles with the impregnation resin so as to be formed into a sheet or tape shape.

The pre-impregnation sheet as conventionally obtained is vulnerable to mechanical stress and thermal stress because the adjacent bundles are bonded together with a non-cured resin so that the bonding strength between the adjacent bundles is susceptibly weakened subject to such stress. As a result of it, as for such conventional pre-impregnation sheet as mentioned above, a long-time storage and a temperature change during storage cause a gap between the adjacent bundles or an interlayer between them to be spaced apart. Further, during transportation and the production of a final product by use of such pre-impregnation sheet, the bonding strength between the adjacent bundles is weakened owing to mechanical stress and thermal stress so as to facilitate a gap or space to be generated between them with detriment to the quality of such sheet and a final product as well.

The widthwise and longitudinal strength of a fibers reinforced plastic product produced by forming a pre-impregnation sheet comprising a plurality of uni-directionally aligned multifilament bundles and curing the impregnation resin depends on the strength of the cured resin itself and the bonding strength between the cured resin and the fibers. As for such conventional pre-impregnation sheet as mentioned above, the bonding strength between the cured resin and the fibers is relatively weak so that the widthwise and longitudinal strength of a fibers reinforced plastic product with such conventional pre-impregnation sheet in use is poor. Especially, the strength of a final product obtained by use of such pre-impregnation sheet as a gap being generated between the adjacent bundles is deteriorated and its finished appearance is poor, in addition to which there occur a lot of inconsistency in quality among final products.

The invention is to provide a pre-impregnation sheet comprising a plurality of fibers bundles aligned with each other and a method of producing the same in which the bonding strength between the adjacent bundles is not deteriorated owing to mechanical stress or thermal stress and a gap is hard to be generated between those bundles.

The invention is to provide a pre-impregnation sheet comprising a plurality of fibers bundles aligned with each other and a method of producing the same sheet wherein during handling and transportation, in process or during storage, its quality is not deteriorated.

The invention is further to provide a pre-impregnation sheet comprising a plurality of multifilament bundles aligned with each other and a method of producing the same wherein the widthwise and longitudinal strength of a fibers reinforced plastic product is enhanced and there is no inconsistency in quality among final products.

The pre-impregnation sheet comprising a plurality of fibers bundles aligned with each other according to the invention is characterized in uni-directionally and adjacently disposing a plurality of multifilament bundles and crosswise intermingling and commingling the monofilaments of those bundles with regard to the longitudinal and latitudinal direction of the fibers bundles and impregnating the bundles as intermingled and commingled with a resin.

The multi-filament bundle in use herein is such that a lot of filaments are converged into a bundle, a yarn or tow comprising a bundle of continuous filaments being preferred herein.

The following conventional fibers are adopted for producing a pre-impregnation sheet according to the invention.
(1) Organic fibers: nylon (in a line of polyamide); rayon (in a line of cellulose); vinylon (in a line of polyvinylalcohol) and so forth
(2) Organic heat-resistant fibers: aromatic polymer; polybenzoimidazole; polyfluorocarbon; polyamide; phenol;

polyphenyleneoxodiazole;bisbenzoimidazobenzophenanthroline; polythiadiazole; polyphenylenetriazole; polybithiazole; polyimide and so forth.

(3) Inorganic fibers: glass fibers; boron nitride fibers; alumina; silicone nitride fibers; asbestos; zirconium; silicone carbide; carbonaceous, graphite, flame resistant carbon fibers and so forth.

(4) Metallic fibers: tungsten alloy; beryllium; copper alloy; ferric and aluminium fibers and so forth.

(5) Complex fibers: boron fibers cored with tungsten fibers; boron carbide cored with tungsten fibers; silicone carbide fibers cored with tungsten and boron fibers and so forth.

(6) Combination comprising more than two fibers as selected from the above (1) to (5), preferably, combined fibers with flexibility and softness.

In order to intermingle the monofilaments of the adjacent bundles and within the same bundle with each other, any adjacent bundles are overlapped one over another to be closely attached together uniform in thickness so as to be formed into a sheet-like or tape shape with a certain width and a high-pressurized fluid is blown to the surface of the respective bundles in alignment with the tensile force of 0.02 to 0.65 g longitudinally applied to the respective bundles to prevent them from being slackened during operation.

The high-pressurized fluid in use includes water, mixture of water and air, an organic solvent such as methylalcohol, ethylalcohol, acetone, toluene, methyl ethyl ketone and so forth and a synthetic resin. In case of synthetic resin being adopted for the fluid, preferably, the same resin as the impregnation resin is used. Upon spraying such synthetic resin, it is preferred to lower the viscosity thereof by heating the same or adding an organic solvent having compatibility with the resin in use or diluents with the exclusion of the organic solvent such as vinyl chrolide resin plasticizer, a higher boiling point solvent, polypropyleneglycole, stylene monomer and polyethylene.

In the case of water, mixture of water and air being adopted for the fluid, it makes blowing operation cost-saving and the relevant facilities structurally simplified as well as does without fluidal adjustment and contamination of job environment while in the case of organic solvent or synthetic resin being adopted for such fluid, it makes drying operation subsequent to blowing operation simplified or does without the former operation so that a matrix resin impregnation operation is performed following the blowing operation. Especially, where the synthetic resin being sufficiently blown to the respective bundles, it does without dipping them into a synthetic resin solution anew and the matrix resin is impregnated with the respective bundles only by pressing those subjected to blowing operation with the rollers.

Herein, a high-pressurized fluid is blown to the respective bundles surface from a nozzle disposed above such surface with an interval therefrom and crosswise with regard to the alignment direction of the respective bundles.

The size of a nozzle aperture, the interval between the nozzle and the bundles surface and the number of nozzles depend on the diameter of the respective monofilaments as well as the thickness of the fibrous layer, but as for the size of the nozzle aperture, it shall be 1 mm or below, preferably, ranging from 0.05 mm to 0.5 mm. The size of the nozzle aperture becoming larger than the above maximum value, a lot of monofilaments are intermingled with each other in simultaneous transposition so as to cause the respective bundles to be put into disorder, which makes the thickness of the respective bundles non-uniform with detriment to the effect brought by aligning the respective bundles with each other.

The interval between the nozzle aperture and the respective bundles surface depends on the pressure by which the fluid is blown to them, the relative moving speed of the respective bundles to the nozzle aperture, the diameter of the respective monofilaments and the thickness of the respective bundles and so forth, which interval preferably ranges from 1

to 15 mm.

The pressure by which the fluid is blown to the respective bundles depends on the size of the nozzle aperture, the interval between the nozzle aperture and the respective bundles surface, the relative moving speed of the respective bundles to the nozzle aperture, the diameter of the respective monofilaments and the thickness of the respective bundles, which pressure preferably ranges from 50 to 400 kg/cm^2. The pressure being less than 50kg/cm^2, the transposition of the respective monofilaments occurs scarcely so as to make the interengagement between the respective bundles insufficient while going beyond 400kg/cm^2, a lot of fluffs occur along with the fibrous cut on the respective bundles.

Upon a high-pressurized fluid being blown over to the respective bundles surface, it may make them move in their alignment direction together with moving them crosswise with regard to their alignment direction with the nozzle fixed in a position while it may as well make the nozzle move with the respective bundles fixed in a position. The moving speed of either the nozzle or the respective bundles preferably ranges from 1 to 10 m/minute. Figure 2 shows a case where the respective bundles are under continuous treatment. As shown, they are endlessly wound up under a certain tension, whereupon the nozzle reciprocally moves crosswise with regard to the wind-up direction so as to discharge high-pressurized fluid towards the respective bundles surface.

The impregnation resin as adopted herein includes such thermoset plastic resins as phenol resin, non-saturated polyester resin, epoxy resin and such heat-resistant resins as polyimide resin, polybenzoimidazole resin, polyphenylen resin and friedel-crafts resin, which resins are heated or to which resins an organic solvent or diluent is added in order to lower the resinous viscosity.

Upon the high-pressurized fluid being blown over to the respective bundles surface, the provision of an abutment plate in the vicinity of the bottom side of the respective bundles

to which such fluid is blown over and in parallel with such surface enables the discharged fluid to be bounced back to be further put into contact with the respective bundles surface, which improves the efficiency of transposing the monofilaments of the respective bundles.

The abutment plate is smooth on the surface so as to throw back the discharged fluid and made from metallic, plastic, glass, wooden, hard rubber material and so forth, which plate is formed into a flat or cylindrical shape with no opening on the surface or may be provided with meshed opening or slit openings as shown in Figures 3 through 6.

The use of the abutment plate enables the respective bundles to be aligned with each other thereon and facilitates the holding means to hold the respective bundles with tension applied thereto to be disposed in a position so that the degree to which the respective monofilaments are intermingled with each other is adjustable in an arbitrary manner.

Then, the invention is explained with reference to the accompanying drawings on the basis of one embodiment to produce a pre-impregnation sheet comprising a plurality of multifilament bundles aligned with each other.

As shown in Figures 1 and 2, a group of respective multifilament bundles 1 aligned with each other is wound up by the wind-up drum 14 from the creel 7, which group is passed through the receptacle 9 with the respective bundles held by the tension control rollers 41, 42 and 43. During the respective bundles being in passage through the receptacle, a high-pressurized fluid is blown over to the respective bundles surface through the nozzle 6 crosswise disposed with regard to the moving course of the bundles and with an interval from the respective bundles surface by driving the pump 8. The receptacle 9 is intended for receiving the fluid blown over to the respective bundles between the rollers 42 and 43 and is provided with an outlet which is not shown in the drawings to circulate the fluid back to the pump 8. Further, the receptacle 9 is provided with an abutment plate 3 disposed along the moving

course of the bundles, which plate is intended for throwing back the discharged fluid to the monofilaments of the respective bundles so as to enhance the transposition of the monofilaments or to make an efficient use of the fluid in use.

The abutment plate shall be arranged such that it throws back a high-pressurized fluid and is provided with physical strength enough to throw back the same. Figure 3 through 6 show such plate formed into a flat and a cylindrical shape. In the case of a number of openings being provided through a flat abutment plate, it facilitates such high-pressurized fluid to pass through the respective bundles so that the monofilaments of the respective bundles are transposed not only crosswise with regard to the moving course of the bundles, but also in the thickness direction of the bundles, which enhances them to be further intermingled with one another.

That is to say, Figure 3 shows a flat abutment plate 3a while Figure 4 showing a flat abutment plate 3b provided with slit openings 5b. Figure 5 shows a flat abutment plate 3c provided with meshed openings 5c. Figure 6 shows a side view of an apparatus wherein a high-pressurized fluid is blown over to the multifilament bundle 1d through the nozzle 6d with the cylindrical abutment plate 3d in use. The abutment plate provided with such openings is appropriate for the production of a pre-impregnation sheet larger in thickness.

Reference numeral 6 indicated in Figures 1 and 2 is a nozzle reciprocally moving crosswise with regard to the moving course of the respective bundles.

A multifilament bundles sheet produced by transposing the monofilaments of the respective bundles widthwise with regard to the alignment direction of the respective bundles and intermingling them with one another by the action of the high-pressurized fluid is moved to a drying chamber 10. Then, such sheet as dried is dipped into a resin impregnation tank 11 for bathing. Subsequently, such sheet as impregnated with a resin is treated with the roller 12 to make the impregnation operation complete and to adjust the amount by which such sheet

is impregnated with the resin. The sheet completed with the impregnation operation is further moved to a heating chamber 13 to volatilize the organic solvent component contained in the impregnation sheet and to enhance the polymerization and condensation of the impregnation resin so as to be wound up around a wind-up roller 14 as a pre-impregnation sheet comprising a plurality of multifilament bundles aligned and commingled with each other. The impregnation sheet to be heat-treated within the heating chamber is preferably sandwiched with releasing sheets.

As shown in Figure 7, the pre-impregnation sheet comprising a plurality of multifilament bundles aligned in parallel and commingled with each other is arranged such that the monofilaments existing between the respective bundles 1e and 1e and a part of or most of those monofilaments 2f within the same bundle are intermingled with each other so that the bonding strength between the respective monofilaments and the resin is not deteriorated by the action of mechanical stress and thermal stress differently from the prior sheet as shown in Figure 8, for which reason there occurs no gap between the respective bundles so as to prevent its quality from deterioration during handling and transportation, in process or during storage. The multifilament bundles sheet impregnated with a resin according to the invention being processed into a fibers reinforced plastic product, there scarcely occurs the deterioration of the fibrous strength in the longitudinal direction thereof. In comparison with the prior product, the fibrous strength both in the alignment direction and in the widthwise direction is intensified by 1.5 to 4 folds.

The preferred embodiment of the invention is described below on the basis of the following examples, to which examples the invention is not limited.

EXAMPLE 1

One hundred multifilament bundles respectively comprising 12,000 carbon monofilaments in the denier designation of 4800, the tensile strength and the elastic

modulus of which bundle are prescribed as 340 Kg/mm^2 and 20t/mm^2 respectively, are aligned with each other on a wooden flat plate with the tension of 0.10g applied to the respective bundles. Water jet stream subject to the following conditions is blown over to the respective bundles in alignment.

Water Jet Stream Conditions

Diameter of nozzle: 0.2 mmϕ

Maximum pressure: 200 kg/cm^2 (40 spouts per minute)

Interval between the nozzle tip and the respective bundles surface: 3 mm

Number of nozzle: one

Moving speed of the nozzle: 4.5 m/minute (moving crosswise with regard to the alignment direction with the jet air blown to the surface over 5 mm at a time to cover the whole width.)

Subsequent to the spraying operation of water jet stream, a part of carbon fibers as treated is sampled for checking the characteristics thereof, but there is no deterioration found in the tensile strength and the elastic modulus thereof in comparison with those checked prior to be subjected to the spraying operation.

There is no rupture strength in the widthwise direction between the bundles prior to the spraying operation, but posterior to such operation such strength works between them by the force of 200g/1 cm in width.

The pre-impregnation sheet as obtained above is dried for two hours under the temperature of 100 degrees Centigrade and dipped into an epoxy resin solution containing an organic solvent of methyl ethyl ketone, which sheet as impregnated with the resin is dried for 15 minutes under the temperature of 120 degrees Centigrade. The pre-impregnation sheets respectively having 0.1 mm in thickness are uni-directionally laminated one over another so as to be formed into a laminated complex sheet having the dimension of 150 mm in length and 80 mm in width and 3 mm in thickness. The tensile strength (σy) in the longitudinal direction of the complex sheet measures at 193 kg/mm^2 while that in the widthwise direction measures at 8.4 kg/mm^2. The ratio

by which the fibers are contained in the complex sheet amounts to 61 %.

EXAMPLE 2

Under the same conditions as the example 1 excepting that the pressure of the water jet stream is set at 400 kg/cm^2, the respective carbon fibers bundles are treated so as to be formed into the respective pre-impregnation sheets, which sheets are laminated one over another so as to be processed into a laminated complex sheet having the same dimension as above. The tensile strength of the complex sheet in the longitudinal measures at 189 kg/mm^2 while that in the widthwise direction measures at 14.1 kg/mm^2.

EXAMPLE 3

Under the same condition as the example 1 excepting that the jet stream comprises a solution containing epoxy resin by 35% and methyl ethyl ketone together with a curing agent, the viscosity of which solution measures at 25 cp at the temperature of 20 degrees Centigrade, the respective carbon fibers bundles are treated so as to be formed into the respective pre-impregnation sheets, which sheets are laminated one over another so as to be processed into a laminated complex sheet having the same dimension as that of the example 1. The tensile strength in the longitudinal direction thereof measures at 194 kg/mm^2 while that in the widthwise direction thereof measures at 7.6 kg/mm^2.

COMPARISON 1

Under the same conditions as the above example 1 excepting that the water jet stream is not used, the respective carbon fibers bundles used in the above example 1 are treated so as to be formed into the respective pre-impregnation sheets, which sheets are laminated one over another so as to be processed into a laminated complex sheet having the same dimension as that of the example 1. The tensile strength in the longitudinal direction thereof measures at 195 kg/mm^2 while that in the widthwise direction thereof measures at 3.8 kg/mm^2.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows one embodiment to carry out the method of producing a pre-impregnation sheet according to the invention; Figure 2 is a perspective view of an apparatus to blow high-pressurized fluid to the respective fibers bundles; Figures 3 through 5 show a plan view of an abutment plate in various shapes; Figure 6 shows a side view of an apparatus blowing a high-pressurized fluid over from a nozzle to the respective fibers bundles with a cylindrical abutment plate in use; Figure 7 shows the longitudinal plan view of a pre-impregnation sheet according to the invention while Figure 8 shows the corresponding view thereof according to the prior art.